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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Paint Binder Granules

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PAINT BINDER GRANULES

A b s t r a c t

Paint binder granules containing at least one cellulose ester A, at least one polymer B and at least one polymerizable monomer C.

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PAINT BINDER GRANULES

This invention relates to free-flowing paint binder granules consisting essentially of cellulose esters and polymers, to a process for their production and to their use in paints, particularly polyurethane paints.

5       The incorporation of cellulose nitrate in polyurethane paints is known to lead to an improvement in a number of applicational properties, including drying rate, pigmentability, gloss and thermoformability.

10       It is now a legal requirement that the cellulose nitrate to be incorporated in polyurethane paints must not be used in pure 100% form because, in its dry state, it can readily be ignited by impact or friction. For this reason, commercially available cellulose nitrates have to be treated either with a non-gelling, liquid moistening agent  
15       in a quantity of at least 25% by weight or with a gelling desensitizing agent in a concentration of at least 18% in order to reduce the dangers during storage and handling and also during transport.

20       Additives of this type lead to considerable problems during the processing of polyurethane paints. Thus, the most common moistening agents for cellulose nitrates are alcohols, such as ethanol, isopropanol or n-butanol, and also water. These moistening agents react with the isocyanates used in polyurethane paints to form low molecular  
25       weight compounds which clearly reduce the quality of the paint film. In addition, an increased content of isocyanates in these paints is necessary in order to be able to saturate the OH groups of the moistening agent.

30       Accordingly, attempts have been made to use solvents inert to isocyanates as moistening agents. According to DE-A-3 041 085, cellulose nitrate moistened with alcohol and/or water is dissolved in a solvent which dissolves the cellulose nitrate or in an azeotropic mixture consisting of

a solvent and a non-solvent. The alcohol and/or the water are then removed from this cellulose nitrate solution by distillation. This process for the production of cellulose nitrates containing liquid hydrocarbon compounds, such as  
5 for example toluene- and xylene-moistened cellulose nitrates, is difficult to handle on safety grounds, for example on account of the electrostatic charging, and is highly cost-intensive. The same also applies to the process described in US-PS 3,284,253 for the production of  
10 cellulose nitrate moistened with a liquid hydrocarbon, the water again being removed by azeotropic distillation.

EP-A-0 172 482 describes a process in which cellulose nitrate is moistened with tert.-butanol, a typical displacement process being used. In order to adjust the water  
15 contents of <0.1% by weight required for the polyurethane paints with this process, the butanol has to be used in an extremely large quantity to displace the water. In addition, tertiary alcohols also react with the isocyanates, albeit at a very slow reaction rate. In addition, butanol  
20 is an undesirable additive in many paint formulations.

In view of the problems created by liquid moistening agents, cellulose nitrates plasticized with plasticizers are often used for polyurethane paints. Dibutyl phthalate or dioctyl phthalate is generally used as the plasticizer  
25 (see DE 1 203 652, DE 1 470 860 and DE 1 570 121). Low molecular weight plasticizers such as these, which do not contain any hydroxyl groups, distinctly reduce the quality of a polyurethane paint film. Because of their high volatility at the high temperatures often applied during  
30 processing, for example in the case of coated aluminium foils, they also lead to deposits on processing machinery and to an increased health risk. According to the prior art, plasticizers containing hydroxyl groups can generally only be incorporated with considerable extra effort, for  
35 example using additional solvents which have to be subse-

quently removed by distillation. The presence of plasticizers in the cellulose nitrate clearly limits the possibility of subsequent paint formulation, especially since additions of plasticizer in polyurethane paints are often unnecessary because the hardness of the system can be adjusted within wide limits solely by the combination of soft and hard resins and various polyisocyanates.

DE 3 836 779 describes a process which uses a cellulose ester/polymer combination prepared from a cellulose ester and at least one polymerizable acrylic acid or acrylate monomer. Cellulose ester polyacrylate granules are formed after polymerization and may even be used in polyurethane paints. These products have the disadvantage of limited compatibility with the hydroxyl-functional polyesters frequently used in polyurethane paints.

DE 2 100 412 describes a process for the production of a cellulose nitrate/polyester polyol mixture. In this process, the polyol is applied to the cellulose nitrate in a mixture of water and solvent in the presence of a protective colloid. The use of solvents involves expensive solvent recycling systems. The protective colloids adversely affect the paint properties to a considerable extent.

In the process described in DE 2 215 624, an aqueous emulsion of a polyol, which acts as a polyurethane prepolymer, is mixed and heated with an aqueous cellulose nitrate suspension in the presence of an emulsifier. After filtration, the filter cake calendered onto a desired layer is dried. This process is confined to polyesters and polyethers of low viscosity which can still be emulsified without difficulty. However, these polyesters and polyethers are soft resins which are only required in special applications of polyurethane paints. Soft, dust-emitting products are formed which are no different in their inflammability from commercially available products. This seriously restricts the usefulness of the products produced by

this process. The large quantity in which the emulsifier is used (at least 3% in the Examples), based on the polyol, leads to a reduction in the water resistance of the films. High-viscosity polyesters having a relatively broad range of applications cannot be produced by this process (see Comparison Example).

The problem addressed by the present invention was to provide cellulose/polymer granules which would not have any of the disadvantages described above and which would be suitable for a broad range of applications, being distinguished in particular by good flow properties, reduced flammability, minimal electrostatic charging and improved paint properties. This problem has surprisingly been solved by applying polymerizable monomers together with polymers to cellulose nitrate and subjecting them to polymerization.

The present invention relates to cellulose ester/polymer granules containing at least one cellulose ester A, at least one polymer B and at least one polymerizable monomer C, an emulsifier content of 0.001 to 2% by weight (based on the sum of components A, B and C) and preferably 0.01 to 1% by weight being used.

Suitable cellulose esters A are cellulose acetobutyrate, cellulose acetate and cellulose nitrate, cellulose nitrate containing 10.0 to 12.6% nitrogen being particularly preferred.

Suitable polymers B are uncrosslinked resins, for example from the following groups: saturated polyesters, unsaturated polyesters, alkyd resins, polyethers, polyacrylates, ketone resins, maleate resins, polycaprolactams, polyurethanes, epoxy resins, polyvinyl resins, amino resins, phenolic resins and silicone resins, more particularly high-viscosity products from these groups. Particularly preferred polymers B are highly viscous, OH-functional polyesters and polyethers, polyurethanes, alkyd resins.

Mixtures of the above-described polymers are also suitable.

Suitable polymerizable monomers C are vinyl monomers, more particularly acrylic and methacrylic acid and derivatives thereof, such as butyl acrylate, butyl methacrylate, hydroxypropyl acrylate, methyl acrylate, methyl methacrylate, ethyl methacrylate, ethyl acrylate, hydroxyethyl acrylate and hydroxybutyl acrylate and also vinyl esters, vinyl chloride and vinylidene chloride, allyl monomers, styrene and substituted styrenes. Acrylates and methacrylates are particularly preferred. Mixtures of various vinyl monomers are also suitable.

The products according to the invention are obtained by application of an aqueous emulsion of the polymers B and the monomers C to an aqueous cellulose ester suspension, followed by polymerization and then by filtration and drying of the solid.

The granules according to the invention preferably contain 10 to 82% by weight and more particularly 30 to 82% by weight cellulose ester A, 10 to 88% by weight and more particularly 20 to 65 % by weight polymer B and 1 to 50 % by weight, preferably 2 to 30 % by weight and more particularly 3 to 20 % by weight monomer C.

The preparation of the aqueous emulsion of polymer B and monomer C is carried out by known methods of emulsification after polymer B has been mixed with monomer C. The emulsification is preferably carried out with addition of suitable emulsifiers by simple stirring of all the constituents. However, dissolvers, ultrasonic mixers, jet mixers and other known emulsifying units and also combinations of these units may be used.

Both ionic and nonionic emulsifiers and mixtures of ionic and nonionic emulsifiers are suitable for emulsification.

To prepare the granules, an aqueous suspension of a cellulose ester is initially introduced and the emulsion of polymer B and monomer C is then added. Polymer B and mono-



mer C may also be added to the cellulose ester, followed by emulsification.

5 After preparation of the emulsion containing the cellulose ester A, the polymer or polymer mixture B and the monomer or monomer mixture C, polymerization is initiated in this system by addition of a suitable initiator and adjustment of the temperature required to initiate the polymerization reaction. Depending on the type of constituents used, the polymerization reaction takes place  
10 under normal pressure or elevated pressure. The polymerization may be carried out both in an inert gas atmosphere and in a normal atmosphere.

The polymerization reaction may be carried out continuously, discontinuously or on the cascade principle.

15 The reaction requires a radical-forming initiator which is added all at once, in portions or continuously.

The initiator may be added in bulk or in solution. Mixtures of several initiators may also be used. Both oil-soluble and water-soluble initiators are suitable, as are  
20 mixtures of water-soluble and oil-soluble initiators. Examples of water-soluble initiators are peroxides, for example potassium peroxodisulfate. Examples of oil-soluble initiators are organic peroxides and hydroperoxides, such as benzoyl peroxide, lauryl peroxide and cyclohexanone hydroperoxide, percarbonates and azo compounds, such as  
25 azodiisobutyronitrile.

The polymerization initiators are used in a quantity of 0.1 to 15% by weight and preferably in a quantity of 0.5 to 10% by weight, based on the sum of the polymerizable  
30 compounds.

The molecular weights and solubilities may be controlled in the usual way by addition of chain transfer agents and regulators. Examples of suitable chain transfer agents are mercaptomethanol, dodecyl mercaptan, mercaptopropionic acid and bis-(isopropylxanthogene) disulfite.  
35



Preferred polymerization temperatures are in the range from 0 to 120°C and preferably in the range from 20 to 80°C. The polymerization time may be between a few minutes and several hours and is preferably in the range from 1 to 8 hours.

In a second step, another monomer or a mixture of monomers may optionally be added to the suspension of granules and polymerized.

The resulting cellulose ester/polymer granules may be separated from the aqueous phase by conventional methods of separation, such as centrifugation or sieving.

Drying may be carried out in conventional drying units, such as for example tray dryers, belt dryers or fluidized bed dryers. The drying temperature should not exceed 120°C, temperatures of 40 to 80°C being preferred.

The resulting granules preferably contain the cellulose ester A, the polymer or polymers B and the polymerized monomer or polymerized monomer mixture C. The products according to the invention have a narrow particle size distribution and excellent flow properties. It is worth noting in this regard that, in general, no fine dust is emitted, so that the danger potential is considerably reduced by comparison with known products containing cellulose esters by virtue of the reduced electrostatic charging.

Compared with commercially available products containing the plasticizers dibutyl phthalate and dioctyl phthalate, the resulting granules show distinctly reduced flammability (see Examples 1 to 10).

In general, the cellulose ester/polymer granules according to the invention are clearly and readily soluble in known solvents or solvent mixtures for cellulose ester binders, more particularly esters and ketones. The cellulose ester/polymer granules according to the invention may be combined with various paint binders and paint

additives and, depending on the composition of the cellulose ester/polymer granules, may then be used for paints intended for a variety of applications, including for example wood, metals, plastics, paper, films, leather and magnetic information storage media. Where OH-functional polyesters and alkyd resins are used as polymer B, they are particularly suitable for polyurethane paints for the above-mentioned applications. For this purpose, they may be combined with a number of polyurethane paint binders both from the group of OH-functional polyesters and alkyd resins and from the group of OH-functional polyacrylates and conventional isocyanates.

However, they are also suitable as additives for other paints, being distinguished by virtue of their polymeric character as particularly migration-stable additives, particularly for coatings which come into contact with foods.

Examples 1 to 10:

General procedure for the production of the paint binder granules

A 50% aqueous emulsion of polymer B and the monomer mixture C is prepared in a stirred glass vessel using a dissolver disc, optionally with addition of a chain transfer agent and emulsifiers. The water containing 1 to 2% by weight emulsifier (based on the total weight of the substances B and C to be emulsified) is initially introduced and the mixture of polymer B, monomer mixture C and the chain transfer agent is then added dropwise. Ethoxylated nonyl phenol containing approx. 50 ethylene oxide units per mol is used as the emulsifier.

Water is added to the cellulose ester in a reaction vessel until a stirrable suspension is obtained (ratio of solid to liquid approx. 1:3.5). The initiator (0.05 to 0.2% by weight based on the total weight of cellulose ester

A, polymer B and monomers C) and then the above-described emulsion in the desired quantity are added to the suspension thus formed and the resulting emulsion is heated to 60°C and left at that temperature until polymerization is complete. Production examples are listed in Table 1.

The granules are filtered under suction and dried at 50°C in a fluidized bed dryer.

Various polymers B (see Table 1) were used:

1. Branched polyester modified with non-drying fatty acids (OH content 4%); Desmophen® 1300, a product of Bayer AG, Leverkusen
2. Branched polyester modified with saturated low molecular weight fatty acid (OH content approx. 5%); Desmophen® RD 181, a product of Bayer AG, Leverkusen
3. Weakly branched polyester (OH content approx. 5%); Desmophen® 1200, a product of Bayer AG, Leverkusen,
4. Medium-oil, non-drying phthalate-based alkyd resin containing 43% synthetic peanut oil (OH content approx. 4%); Rokraplast® E 420, a product of Robert Kraemer, Bremen.

The trademarks are used in the following.

The burning rate is determined via the flame propagation in a 10 cm long metal channel filled with 1 g of the product to be tested. To this end, the product is ignited at one end and the time which the fire takes to reach the opposite end is measured. The burning time of a commercially available cellulose nitrate of the standard 34 E type containing 18% dibutyl phthalate (Walsroder Nitrocellulose-Chips E 330) of < 1 s was used as reference.

For performance testing, the products were dissolved to form a 25% by weight solution in a solvent mixture (ethyl methyl ketone/methyl isobutyl ketone/xylene/cyclohexanone = 1:1:1.8:0.2 part by volume) and evaluated for clear solubility.

To evaluate hardening behavior, 6 parts by weight

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5 polyisocyanate Desmodur N, a product of Bayer AG, Leverkusen,  
per 100 parts by weight paint were added to the solutions  
which were then applied to a glass plate in a layer thickness  
of 180  $\mu\text{m}$ . Pendulum hardness according to DIN 53 157 and  
water resistance according to DIN 53 168 are determined  
after a hardening time of 18 hours at room temperature.

Table 1

Test number	1	2	3	4	5	6	7	8	9	10
<u>Cellulose ester A:</u>										
Nitrocellulose, standard type 34 E (% by wt.)	70		70	70	70	70	70		80	60
Nitrocellulose, standard type 27 A (% by wt.)		70								
Cellulose acetobutyrate (% by wt.)								70		
<u>Polymers B:</u>										
Desmophen 1300 (% by wt.)	24	27	21	27				27	17.9	36
Desmophen RD 181 (% by wt.)					27					
Desmophen 1200 (% by wt.)						27				
Rokraplast AE 420 (% by wt.)							27			
<u>Monomers C:</u>										
Butyl acrylate (% by wt.)	5	2.5	7.5	2.9	2.5	2.5	2.5	2.6	2.0	3.3
Bis-(isopropylxanthogene)-disulfite (% by wt.)	0.0006	0.03	0.009	0.03	0.003	0.003	0.003	0.003	0.002	0.04
Hydroxypropyl methacrylate (% by wt.)	1	0.5	1.5	0.1	0.5	0.5	0.5	0.4	0.1	0.7
Emulsifier (based on A, B, C) (% by wt.)	0.3	0.5	0.3	0.5	0.3	0.3	0.3	0.3	0.25	0.7
Clear solubility	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
Non-volatile component	99.3	99.2	99.3	99.4	99.3	99.2	99.3	99.5	99.1	99.4

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Table 1 (continued)

Test number	1	2	3	4	5	6	7	8	9	10
Burning time (s)	7.5	11	7.0	6.2	5.1	4.5	4.2	4.0	3	9
Pendulum hardness, DIN 53 157 (s)	201	183	198	190	185	180	176	179	195	170
Water resistance, DIN 53 168	passed	passed	passed	passed	passed	passed	passed	passed	passed	passed

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CLAIMS

1. Paint binder granules containing at least one cellulose ester A, at least one polymer B and at least one polymerizable monomer C.
- 5 2. Paint binder granules as claimed in claim 1, characterized in that the cellulose ester contains cellulose acetobutyrate and/or cellulose nitrate in a concentration of 10 to 82% by weight.
- 10 3. Paint binder granules as claimed in claim 1 or 2, characterized in that they contain a polymer B in a concentration of 10 to 88% by weight.
4. Paint binder granules as claimed in any of claims 1 to 3, characterized in that they contain 1 to 50% by weight of a polymerized monomer C or a mixture of monomers C.
- 15 5. Paint binder granules as claimed in any of claims 1 to 4, characterized in that the monomers C are vinyl compounds.
6. Paint binder granules as claimed in any of claims 1 to 5, characterized in that the monomers C are acrylic acid and/or methacrylic acid or derivatives of these acids.
- 20 7. A process for the production of the paint binder granules claimed in any of claims 1 to 6, characterized in that an aqueous emulsion of the polymers B and the monomers C is applied to an aqueous cellulose ester suspension, the monomers C are polymerized using initiator and the resulting product is filtered and dried.
- 25 8. The use of the paint binder granules claimed in any of claims 1 to 6 for the production of paints.
9. The use claimed in claim 8, characterized in that
- 30 polyurethane paints are produced.

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